Supporting information

Pd-Catalyzed regio- and stereoselective allylic substitution of vinylethylene carbonates with 1,2,4-triazoles

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General experimental details

Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates (Yantai Jiangyou Silica Gel Development Co., Ltd., silica gel HSGF 254). Preparative column chromatography employing silica gel (Qingdao Shenghai Fine Silica Gel Chemical Co., Ltd., 200-300 mesh) was performed according to the method of Still. High-resolution mass spectra (HRMS) were performed at Instrumental Analysis Center of Shanghai Jiao Tong University using ESI method. Proton nuclear magnetic resonance (\(^1\)H NMR) spectra were recorded with a Bruker AVANCE III HD 500 (500 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from trimethylsilane or deuterated water and ppm relative to the center of the singlet at 7.26 ppm for deuteriochloroform, or ppm relative to the center of the quintet at 3.34 ppm for deuteriomethanol. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (\(^{13}\)C NMR) spectra were recorded with a Bruker AVANCE III HD 500 (125 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, ppm relative to the center of the triplet at 77.0 ppm for deuteriochloroform and ppm relative to the center of the septet at 49.54 ppm for deuteriomethanol. \(^{13}\)C NMR spectra were routinely run with broadband decoupling. All of the palladium sources and phospine ligands were purchased from Sinocompound Co. and used as received.
General procedure for the synthesis of substituted 1,2,4-triazoles (2p-2r)

1,2,4-Triazoles 2p-2r were synthesized according to reported procedure, all characterization data are in accordance with literature.1

General procedure for Pd-catalyzed allylic amination of vinylethylene carbonates 1a with 1,2,4-triazoles 2a

To an oven dried screw-cap reaction tube equipped with a magnetic stir bar, Pd2(dbaj)3CHCl3 (5.2 mg, 0.005 mmol, 2.5 mol%), DPPE (3.98 mg, 0.02 mmol, 5 mol%), Ph-VEC 1a (38.0 mg, 0.2 mmol) and 1,2,4-Triazole 2a (20.7 mg, 0.3 mmol) were added. The reaction tube was sealed with rubber-septum, then evacuated and backfilled with nitrogen (this process was repeated a total of three times). Anhydrous THF (2 mL) was added via syringe. The resulting mixture was stirred at 40 ºC for 18 h. The reaction mixture was cooled to room temperature and the solvent was removed by rotary evaporation under vacuum. The crude product was purified by flash column chromatography on silica gel to afford the corresponding product 3a.

(Z)-2-phenyl-4-(1H-1,2,4-triazol-1-yl)but-2-en-1-ol

Yield: 96% (41.3 mg); light yellow solid; (Z:E = 20:1); Purification: petroleum ether/EtOAc = 1:1; 1H NMR (500 MHz, CDCl3) δ 8.13 (s, 1H), 7.92 (s, 1H), 7.48–7.46 (m, 2H), 7.36–7.28 (m, 3H), 5.99 (t, J = 7.8 Hz, 1H), 5.04 (d, J = 7.8 Hz, 2H), 4.67 (s, 2H), 4.31 (bs, 1H); 13C NMR (125 MHz, CDCl3) δ 151.9, 146.1, 142.9, 140.0, 128.5, 128.1, 126.3, 59.8, 46.8, 46.8; HRMS (ESI-MS): Calcd. for C12H13N3O (M+Na): 238.0956, Found: 238.0961.

(Z)-2-(p-tolyl)-4-(1H-1,2,4-triazol-1-yl)but-2-en-1-ol

Yield: 93% (42.6 mg); light yellow oil; (Z:E = >20:1); Purification: petroleum ether/EtOAc = 2:1; 1H NMR (500 MHz, CDCl3) δ 8.12 (s, 1H), 7.92 (s, 1H), 7.36 (d, J = 10.2 Hz, 2H), 7.14 (d, J = 9.8 Hz, 2H), 5.97 (t, J = 9.6 Hz, 1H), 5.02 (d, J = 9.8 Hz, 2H), 4.65 (s, 2H), 3.92 (bs, 1H), 2.33 (s, 3H); 13C NMR (125 MHz, CDCl3) δ 152.0, 146.0, 143.0, 138.0, 137.0, 129.2, 126.2, 121.4, 59.8, 46.8, 21.0; HRMS (ESI-MS): Calcd. for C13H15N3O (M+Na): 252.1113, Found: 252.1108.

(Z)-2-(2-methoxyphenyl)-4-(1H-1,2,4-triazol-1-yl)but-2-en-1-ol
Yield: 83% (40.7 mg); light yellow oil; (Z:E = >20:1); Purification: petroleum ether/EtOAc = 1:1; $^1$H NMR (500 MHz, CDCl$_3$) δ 8.19 (s, 1H), 7.95 (s, 1H), 7.31–7.27 (m, 1H), 7.14 (dd, $J = 9.2, 2.2$ Hz, 1H), 6.96–6.89 (m, 2H), 5.85 (t, $J = 9.2$ Hz, 1H), 5.09 (d, $J = 9.2$ Hz, 2H), 4.49 (s, 2H), 3.86 (s, 3H), 3.00 (bs, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 156.2, 151.9, 145.2, 143.0, 130.3, 130.0, 129.3, 125.4, 121.0, 110.6, 60.9, 55.5, 47.0; HRMS (ESI-MS): Calcd. for C$_{13}$H$_{12}$N$_2$O (M+Na): 268.1062, Found: 268.1055.

(Z)-2-(3-methoxyphenyl)-4-(1H-1,2,4-triazol-1-yl)but-2-en-1-ol

Yield: 90% (44.1 mg); yellow oil; (Z:E = >20:1); Purification: petroleum ether/EtOAc = 3:1; $^1$H NMR (500 MHz, CDCl$_3$) δ 8.13 (s, 1H), 7.93 (s, 1H), 7.28–7.23 (m, 1H), 7.05–7.00 (m, 2H), 6.84 (dd, $J = 10.4, 3.1$ Hz, 1H), 5.99 (t, $J = 9.6$ Hz, 1H), 5.04 (d, $J = 9.6$ Hz, 2H), 4.64 (s, 2H), 3.79 (s, 3H), 4.47 (bs, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 159.6, 152.0, 145.9, 143.0, 141.5, 129.5, 122.5, 118.8, 113.4, 112.2, 59.9, 55.2, 46.8; HRMS (ESI-MS): Calcd. for C$_{13}$H$_{12}$N$_2$O (M+Na): 268.1062, Found: 268.1059.

(Z)-2-(4-methoxyphenyl)-4-(1H-1,2,4-triazol-1-yl)but-2-en-1-ol

Yield: 93% (45.6 mg); light yellow solid; (Z:E = >20:1); Purification: petroleum ether/EtOAc = 1:1; $^1$H NMR (500 MHz, CDCl$_3$) δ 8.12 (s, 1H), 7.92 (s, 1H), 7.41 (d, $J = 8.8$ Hz, 2H), 7.86 (d, $J = 8.8$ Hz, 2H), 5.93 (t, $J = 7.8$ Hz, 1H), 5.01 (d, $J = 7.8$ Hz, 2H), 4.64 (s, 2H), 4.32 (bs, 1H), 3.79 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 159.5, 151.9, 145.4, 142.8, 132.2, 127.5, 120.5, 113.8, 59.7, 55.2, 46.8; HRMS (ESI-MS): Calcd. for C$_{13}$H$_{15}$N$_2$O (M+H): 246.1243, Found: 246.1272.

(Z)-2-(4-fluorophenyl)-4-(1H-1,2,4-triazol-1-yl)but-2-en-1-ol

Yield: 95% (44.6 mg); light yellow oil; (Z:E = 20:1); Purification: petroleum ether/EtOAc = 2:1; $^1$H NMR (500 MHz, CDCl$_3$) δ 8.15 (s, 1H), 7.95 (s, 1H), 7.48–7.44 (m, 2H), 7.02 (dd, $J = 8.7, 8.6$ Hz, 2H), 5.93 (t, $J = 7.9$ Hz, 1H), 5.03 (d, $J = 7.9$ Hz, 2H), 4.65 (s, 2H), 4.08 (bs, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$)
δ 163.7, 161.7, 152.2, 145.6, 143.0, 136.3, 136.2, 128.2, 128.1, 122.1, 115.5, 115.4, 59.9, 46.7; 19F NMR (376 MHz, CDCl3) δ -1.13.72; HRMS (ESI-MS): Calcd. for C12H12F1O (M+H): 234.1043, Found: 234.1046.

(Z)-2-(4-chlorophenyl)-4-(1H-1,2,4-triazol-1-yl)but-2-en-1-ol

![Z-2-(4-chlorophenyl)-4-(1H-1,2,4-triazol-1-yl)but-2-en-1-ol](image)

Yield: 95% (44.8 mg); light yellow oil; (Z:E = 17:1); Purification: petroleum ether/EtOAc = 1:1; 1H NMR (500 MHz, CDCl3) δ 8.14 (s, 1H), 7.95 (s, 1H), 7.41 (d, J = 10.6 Hz, 2H), 7.30 (d, J = 10.8 Hz, 2H), 5.99 (t, J = 9.8 Hz, 1H), 5.04 (d, J = 9.8 Hz, 2H), 4.64 (s, 2H), 3.36 (bs, 1H); 13C NMR (125 MHz, CDCl3) δ 152.1, 145.3, 143.02, 138.5, 134.0, 128.6, 127.7, 122.6, 59.7, 46.6; HRMS (ESI-MS): Calcd. for C12H12ClF1O (M+H): 250.0747, Found: 250.0733.

(Z)-2-(3-bromophenyl)-4-(1H-1,2,4-triazol-1-yl)but-2-en-1-ol

![Z-2-(3-bromophenyl)-4-(1H-1,2,4-triazol-1-yl)but-2-en-1-ol](image)

Yield: 97% (56.8 mg); light yellow oil; (Z:E = 13:1); Purification: petroleum ether/EtOAc = 1:1; 1H NMR (500 MHz, CDCl3) δ 8.15 (s, 1H), 7.96 (s, 1H), 7.62 (dd, J = 4.6, 2.4 Hz, 1H), 7.44–7.39 (m, 2H), 7.20 (d, J = 9.9, 9.8 Hz, 1H), 6.00 (t, J = 9.8 Hz, 1H), 5.05 (d, J = 9.8 Hz, 2H), 4.64 (s, 2H), 3.57 (bs, 1H); 13C NMR (125 MHz, CDCl3) δ 152.1, 145.2, 143.0, 142.3, 131.0, 130.0, 129.4, 125.0, 123.3, 122.6, 59.7, 46.6; HRMS (ESI-MS): Calcd. for C12H12BrF1O (M+H): 294.0242, Found: 294.0237.

(Z)-2-(4-bromophenyl)-4-(1H-1,2,4-triazol-1-yl)but-2-en-1-ol

![Z-2-(4-bromophenyl)-4-(1H-1,2,4-triazol-1-yl)but-2-en-1-ol](image)

Yield: 94% (55.1 mg); light yellow solid; 108-110 °C; (Z:E = >20:1); Purification: petroleum ether/EtOAc = 1:1; 1H NMR (500 MHz, CDCl3) δ 8.14 (s, 1H), 7.95 (s, 1H), 7.46 (d, J = 8.6 Hz, 2H), 7.35 (d, J = 8.6 Hz, 2H), 6.00 (t, J = 7.9 Hz, 1H), 5.03 (d, J = 7.8 Hz, 2H), 4.64 (s, 2H), 4.24 (bs, 1H); 13C NMR (125 MHz, CDCl3) δ 152.1, 145.4, 143.0, 139.0, 131.6, 1278.0, 122.6, 122.2, 59.6, 46.6; HRMS (ESI-MS): Calcd. for C12H12BrF1O (M+H): 294.0242, Found: 294.0256.

(Z)-2-(3,4-dichlorophenyl)-4-(1H-1,2,4-triazol-1-yl)but-2-en-1-ol
Yield: 90% (50.9 mg); yellow oil; (Z:E = 10:1); Purification: petroleum ether/EtOAc = 1:1; ^1H NMR (500 MHz, CDCl$_3$) δ 8.16 (s, 1H), 7.96 (s, 1H), 7.58 (d, $J$ = 2.6 Hz, 1H), 7.41–7.37 (m, 1H), 7.33–7.30 (m, 1H), 6.02 (t, $J$ = 9.8 Hz, 1H), 5.05 (d, $J$ = 9.8 Hz, 2H), 4.62 (s, 2H), 3.54 (bs, 1H); ^13C NMR (125 MHz, CDCl$_3$) δ 152.2, 144.4, 143.0, 140.1, 132.6, 132.1, 130.4, 128.3, 125.7, 123.5, 59.5, 46.5; HRMS (ESI-MS): Calcd. for C$_{13}$H$_{11}$ClN$_3$O (M+H): 284.0357, Found: 284.0352.

(Z)-2-(benzo[d][1,3]dioxol-4-yl)-4-((1H-1,2,4-triazol-1-yl)but-2-en-1-ol

Yield: 89% (46.1 mg); yellow oil; (Z:E = 20:1); Purification: petroleum ether/EtOAc = 2:1; ^1H NMR (500 MHz, CDCl$_3$) δ 8.14 (s, 1H), 7.94 (s, 1H), 6.98–6.95 (m, 2H), 6.77 (d, $J$ = 10.7 Hz, 1H), 5.94 (s, 2H), 5.91 (t, $J$ = 9.8 Hz, 1H), 5.01 (d, $J$ = 9.8 Hz, 2H), 4.61 (s, 2H), 4.28 (bs, 1H); ^13C NMR (125 MHz, CDCl$_3$) δ 151.9, 147.8, 147.5, 145.8, 142.9, 134.2, 121.1, 120.1, 108.2, 106.8, 101.1, 59.8, 46.8; HRMS (ESI-MS): Calcd. for C$_{13}$H$_{11}$N$_3$O$_2$ (M+Na): 282.0855, Found: 282.0854.

(Z)-2-(naphthalen-1-yl)-4-((1H-1,2,4-triazol-1-yl)but-2-en-1-ol

Yield: 79% (41.9 mg); light yellow oil; (Z:E = 20:1); Purification: petroleum ether/EtOAc = 2:1; ^1H NMR (500 MHz, CDCl$_3$) δ 8.15 (s, 1H), 7.97 (s, 1H), 7.89–7.83 (m, 2H), 7.78 (d, $J$ = 8.2 Hz, 1H), 7.49–7.44 (m, 2H), 7.42–7.39 (m, 1H), 7.30 (dd, $J$ = 7.0, 1.4 Hz, 1H), 5.85 (t, $J$ = 7.8 Hz, 1H), 5.15 (d, $J$ = 7.8 Hz, 2H), 4.65 (s, 2H), 3.98 (bs, 1H); ^13C NMR (125 MHz, CDCl$_3$) δ 152.0, 146.5, 142.9, 138.8, 133.6, 131.0, 128.4, 128.1, 126.3, 125.9, 125.5, 125.2, 125.1, 125.0, 62.2, 46.6; HRMS (ESI-MS): Calcd. for C$_{16}$H$_{13}$N$_3$O (M+H): 266.1293, Found: 266.1287.

(Z)-2-(naphthalen-2-yl)-4-((1H-1,2,4-triazol-1-yl)but-2-en-1-ol

S6
Yield: 94% (49.8 mg); light brown solid; \(Z:E = 20:1\); Purification: petroleum ether/EtOAc = 1:1; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.10 (s, 1H), 7.94 (s, 1H), 7.93 (s, 1H), 7.81–7.76 (m, 3H), 7.55 (dd, \(J = 10.7, 2.3\) Hz, 1H), 7.48–7.43 (m, 2H), 6.09 (t, \(J = 9.7\) Hz, 1H), 5.02 (d, \(J = 9.8\) Hz, 2H), 4.74 (s, 2H), 4.30 (bs, 1H); \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 151.9, 146.0, 142.9, 137.2, 133.2, 132.9, 128.1, 128.1, 127.5, 126.3, 126.2, 125.5, 124.2, 122.6, 59.8, 46.8; HRMS (ESI-MS): Calcd. for C\(_{16}\)H\(_{11}\)N\(_3\)O (M+Na): 288.1113, Found: 288.1108.

\((Z)-4-(1H-1,2,4-triazol-1-yl)but-2-en-1-ol\)

Yield: 53% (14.7 mg); light yellow oil; \(Z:E = 5:1, l:b = 1.3:1\); Purification: petroleum ether/EtOAc = 1:1; \(^1\)H NMR (500 MHz, CDCl\(_3\)) for \(Z\) isomer: \(\delta\) 8.13 (s, 1H), 7.94 (s, 1H), 6.03–5.97 (m, 1H), 5.77–5.70 (m, 1H), 4.92 (d, \(J = 9.1\) Hz, 2H), 4.33 (d, \(J = 7.0\) Hz, 2H), 3.18 (bs, 1H); \(^1\)H NMR (500 MHz, CDCl\(_3\)) for \(E\) isomer: \(\delta\) 8.11 (s, 1H), 7.94 (s, 1H), 5.93–5.91 (m, 2H), 4.80 (d, \(J = 5.3\) Hz, 2H), 4.19 (d, \(J = 1.7\) Hz, 2H), 2.56 (bs, 1H); \(^13\)C NMR (125 MHz, CDCl\(_3\)) for \(Z\) isomer: \(\delta\) 151.7, 142.6, 135.0, 123.8, 58.0, 46.2; \(^13\)C NMR (125 MHz, CDCl\(_3\)) for \(E\) isomer: \(\delta\) 151.6, 142.7, 135.4, 123.0, 61.8, 51.0; HRMS (ESI-MS): Calcd. for C\(_{16}\)H\(_{11}\)N\(_3\)O (M+H): 140.0824, Found: 140.0809.

\(2-(1H-1,2,4-triazol-1-yl)but-3-en-1-ol\)

Yield: 40% (11.2 mg); light yellow oil; Purification: petroleum ether/EtOAc = 5:1; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.13 (s, 1H), 7.92 (s, 1H), 6.07 (ddd, \(J = 17.4, 10.5, 7.1\) Hz, 1H), 5.42 (d, \(J = 10.5\) Hz, 1H), 5.30 (d, \(J = 17.2\) Hz, 1H), 4.91 (dd, \(J = 6.9, 3.0, 1.2\) Hz, 1H), 4.14–3.94 (m, 2H), 3.83 (s, 1H); \(^13\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 151.6, 143.1, 132.0, 120.4, 64.5, 64.0; HRMS (ESI-MS): Calcd. for C\(_{16}\)H\(_{11}\)N\(_3\)O (M+H): 140.0824, Found: 140.0818.

\((Z)-2-methyl-4-(1H-1,2,4-triazol-1-yl)but-2-en-1-ol\)

Yield: 32% (9.8 mg); light yellow oil; \(Z:E = 17:1, l:b = 1:3\); Purification: petroleum ether/EtOAc = 2:1; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.09 (s, 1H), 7.94 (s, 1H), 5.54 (t, \(J = 7.8\) Hz, 1H), 4.87 (d, \(J = 7.8\) Hz, 2H), 4.26 (s, 2H), 3.70 (bs, 1H), 1.88 (s, 3H); \(^13\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 151.9, 143.8, 142.7, 119.2, 61.4, 46.3, 22.0; HRMS (ESI-MS): Calcd. for C\(_9\)H\(_6\)N\(_3\)O (M+H): 154.0980, Found: 154.0975.

\(2\text{-methyl-2-}(1H-1,2,4-triazol-1-yl)but-3-en-1-ol\)
Yield: 51% (15.7 mg); light yellow oil; Purification: petroleum ether/EtOAc = 5:1; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.15 (s, 1H), 8.01–7.64 (m, 1H), 6.14 (dd, \(J = 17.5, 10.8\) Hz, 1H), 5.39 (d, \(J = 10.8\) Hz, 1H), 5.20 (d, \(J = 17.5\) Hz, 1H), 4.13 (bs, 1H), 3.99 (d, \(J = 11.8\) Hz, 1H), 3.85 (d, \(J = 11.3\) Hz, 1H), 1.69 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 151.1, 142.2, 137.6, 117.4, 68.4, 65.6, 21.7; HRMS (ESI-MS): Calcd. for C\(_{18}\)H\(_{14}\)NO (M+H): 254.0980, Found: 254.0975.

(Z)-2-phenyl-4-(3-phenyl-1\(\text{H}\)-1,2,4-triazol-1-yl)but-2-en-1-ol

Yield: 96% (55.9 mg); light yellow oil; (Z:E > 20:1); Purification: petroleum ether/EtOAc = 1:1; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.13 (s, 1H), 8.05–7.03 (m, 2H), 7.51–7.49 (m, 2H), 7.44–7.37 (m, 3H), 7.36–7.28 (m, 3H), 6.05 (t, \(J = 8.0\) Hz, 1H), 5.03 (d, \(J = 8.1\) Hz, 2H), 4.72 (s, 2H), 4.47 (bs, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 163.0, 146.8, 143.8, 140.2, 130.3, 129.5, 128.7, 128.5, 128.2, 126.3, 126.3, 122.2, 60.0, 46.8; HRMS (ESI-MS): Calcd. for C\(_{18}\)H\(_{17}\)NO (M+H): 292.1450, Found: 292.1445.

(E)-4-(3-(4-methoxyphenyl)-1\(\text{H}\)-1,2,4-triazol-1-yl)-2-phenylbut-2-en-1-ol

Yield: 96% (61.7 mg); light yellow oil; (Z:E = 5:1); Purification: petroleum ether/EtOAc = 2:1; \(^1\)H NMR (500 MHz, CDCl\(_3\)) for Z isomer: \(\delta\) 8.09 (s, 1H), 7.98–7.94 (m, 2H), 7.51–7.49 (m, 2H), 7.36–7.28 (m, 3H), 6.95–7.92 (m, 2H), 6.05 (t, \(J = 8.0\) Hz, 1H), 5.01 (d, \(J = 8.0\) Hz, 2H), 4.70 (d, \(J = 4.6\) Hz, 2H), 4.56 (dd, \(J = 6.0, 6.0\) Hz, 1H), 3.83 (s, 3H); \(^1\)H NMR (500 MHz, CDCl\(_3\)) for E isomer: \(\delta\) 7.94 (s, 1H), 7.60–7.58 (m, 2H), 7.51–7.49 (m, 2H), 7.36–7.28 (m, 3H), 7.04–7.03 (m, 2H), 6.02 (t, \(J = 7.8\) Hz, 1H), 5.05 (d, \(J = 7.9\) Hz, 2H), 4.65 (d, \(J = 5.0\) Hz, 2H), 4.27 (dd, \(J = 6.6, 4.3\) Hz, 1H), 3.87 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) for Z isomer: \(\delta\) 162.9, 160.6, 146.8, 143.6, 140.3, 128.5, 128.4, 128.1, 127.7, 126.3, 122.2, 114.0, 59.9, 55.3, 46.7; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) for E isomer: \(\delta\) 161.2, 154.7, 150.9, 146.3, 140.4, 130.3, 128.0, 126.4, 123.0, 122.8, 119.8, 114.4, 60.0, 55.4, 46.4; HRMS (ESI-MS): Calcd. for C\(_{18}\)H\(_{16}\)ClNO (M+H): 322.1256, Found: 322.1245.

(Z)-4-(3-(4-chlorophenyl)-1\(\text{H}\)-1,2,4-triazol-1-yl)-2-phenylbut-2-en-1-ol

Yield: 96% (59.9 mg); light yellow oil; (Z:E = 20:1); Purification: petroleum ether/EtOAc = 1:1; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.14 (s, 1H), 7.97 (d, \(J = 8.6\) Hz, 2H), 7.51–7.49 (m, 2H), 7.39 (d, \(J = 8.6\) Hz, 2H), 7.37–7.29 (m, 3H), 6.06 (t, \(J = 8.0\) Hz, 1H), 5.05 (d, \(J = 8.0\) Hz, 2H), 4.72 (s, 2H), 4.20 (dd, \(J = 6.3, 6.2\) Hz, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 162.1, 146.9, 143.9,
Procedure for gram scale reaction of 3a

To an oven dried screw-cap reaction tube equipped with a magnetic stir bar, Pd₂(dba)₃·CHCl₃ (0.156 g, 0.15 mmol, 2.5 mol%), DPPE (0.119 g, 0.30 mmol, 5 mol%), Ph-VEC 1a (1.140 g, 6.0 mmol) and 1,2,4-triazole 2a (0.621 g, 9.0 mmol) were added. The reaction flask was sealed with rubber-septum, then evacuated and backfilled with nitrogen (this process was repeated a total of three times). Anhydrous THF (30 mL) was added via syringe. The resulting mixture was stirred at 40 ºC for 18 h. The reaction mixture was cooled to room temperature and the solvent was removed by rotary evaporation under vacuum. The crude product was purified by flash column chromatography on silica gel to afford the corresponding product 3a as light yellow solid in 91% (1.174 g) and Z:E = >20:1.

Procedure for Dess-Martin oxidation of 3a

(Z)-2-phenyl-4-(1H-1,2,4-triazol-1-yl)but-2-enal

A screw-capped vial was charged with the 3a (43.0 mg, 0.2 mmol), DMP (93.3 mg, 0.220 mmol, 1.10 equiv.), CH₂Cl₂ (5 mL). The reaction mixture was stirred for 3 hours at room temperature. The mixture reaction washed twice with a saturated solution (5 mL) of NaHCO₃/Na₂S₂O₃ (1:1). And then the liquid was extracted with CH₂Cl₂ three times. After drying over Na₂SO₄ for 30 minutes, the combined organic phase was concentrated by evaporated under reduced pressure, and then the residue was purified by chromatography on silica gel to afford 5 as yellow oil in 75% yield (34.4 mg).² (Z:E = >20:1); Purification: petroleum ether/EtOAc = 3:1; ¹H NMR (500 MHz, CDCl₃) δ 9.70 (s, 1H), 8.05 (s, 1H), 7.00 (s, 1H), 7.49–7.42 (m, 3H), 7.24–7.22 (m, 2H), 6.83 (t, J = 6.5 Hz, 1H), 5.08 (d, J = 6.4 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 192.1, 152.5, 145.6, 144.0, 143.0, 130.8, 129.1, 129.0, 128.7, 47.8; HRMS (ESI-MS): Calcd. for C₁₂H₁₁N₂O (M+H): 294.0980, Found: 294.0977.
Procedure for carbamate synthesis from 3a

\[
\text{3a} \quad \xrightarrow{\text{4-MeO-phenyl isocyanate}} \quad \text{6}
\]

91% yield  
Z:E = >20:1

\[
\text{3a} \quad \xrightarrow{\text{PhCOCl, NaH}} \quad \text{7}
\]

87% yield  
Z:E = >20:1

(Z)-2-phenyl-4-(1H-1,2,4-triazol-1-yl)but-2-en-1-yl(4-methoxyphenyl)carbamate

A screw-capped vial was charged with the 3a (43.0 mg, 0.2 mmol), 4-MeO-phenyl isocyanate (35.8 mg, 0.240 mmol, 1.2 equiv.), Et$_3$N (36.2 µL, 0.260 mmol, 1.3 equiv.) and THF (2.0 mL). The reaction mixture was stirred for 16 hours under N$_2$ at 40 ºC. After filtration, the mixture was extracted with EtOAc, dried over anhydrous Na$_2$SO$_4$, and the solvent was removed in vacuum. The crude product was purified by flash column chromatography on silica gel to get the desired product 6 as light yellow oil in 91% yield (66.3 mg). (Z:E = >20:1); Purification: petroleum ether/EtOAc = 1:1; $^1$H NMR (500 MHz, CDCl$_3$) δ 9.70 (s, 1H), 8.18 (s, 1H), 7.95 (s, 1H), 7.44–7.42 (m, 2H), 7.36–7.31 (m, 3H), 7.27–7.21 (m, 2H), 7.07 (bs, 1H), 6.85–6.81 (m, 2H), 6.12 (t, $J = 7.0$ Hz, 1H), 5.18 (s, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 156.0, 153.6, 151.9, 143.0, 139.3, 138.8, 130.6, 128.6, 128.3, 126.4, 125.8, 120.7, 114.2, 61.0, 55.4, 47.4; HRMS (ESI-MS): Calcd. for C$_{20}$H$_{20}$N$_4$O$_3$ (M+H): 365.1614, Found: 365.1604.

Procedure for ester synthesis from 3a

(Z)-2-phenyl-4-(1H-1,2,4-triazol-1-yl)but-2-en-1-yl benzoate

A screw-capped vial was charged with the 3a (43.0 mg, 0.2 mmol), benzoyl chloride (30.2 µL, 0.260 mmol, 1.3 equiv.), NaH (10.4 mg, 0.433 mmol, 1.3 equiv.) and THF (2.0 mL). The reaction mixture was initially stirred at 0 ºC for 30 minutes and then stirred under N$_2$ atmosphere at room temperature for 24
hours. After filtration, the mixture was extracted with EtOAc, dried over anhydrous Na₂SO₄, and the solvent was removed in vacuum. The crude product was purified by flash column chromatography on silica gel to get the target product 7 as colorless oil in 87% yield (55.5 mg). (Z:E = >20:1); Purification: petroleum ether/EtOAc = 7:3; ¹H NMR (500 MHz, CDCl₃) δ 8.20 (s, 1H), 7.97 (s, 1H), 7.96–7.94 (m, 2H), 7.57–7.54 (m, 1H), 7.50–7.48 (m, 2H), 7.43–7.40 (m, 2H), 7.39–7.32 (m, 3H), 6.20 (t, J = 7.0 Hz, 1H), 5.38 (s, 2H), 7.05 (d, J = 6.4 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 166.3, 152.2, 143.0, 139.0, 139.0, 133.3, 129.6, 129.6, 128.5, 128.4, 126.4, 126.2, 61.3, 47.6; HRMS (ESI-MS): Calcd. for C₁₉H₁₇N₃O₂ (M+H): 320.1399, Found: 320.1405.

**Procedure for Hydrogenation of 3a**

A screw-capped vial was charged with the 3a (43.0 mg, 0.2 mmol), the Pd/C (10%) catalyst (2.1 mg, 10 mol%) and MeOH (2.0 mL). The reaction mixture was stirred for 12 hours under H₂ at room temperature. After filtration, the mixture was extracted with EtOAc, dried over anhydrous Na₂SO₄, and the solvent was removed in vacuum. The crude product was purified by flash column chromatography on silica gel to afford 8 as colorless oil in 95% yield (41.2 mg).¹ Purification: petroleum ether/EtOAc = 1:2; ¹H NMR (500 MHz, CDCl₃) δ 7.87 (s, 1H), 7.83 (s, 1H), 7.36–7.33 (m, 2H), 7.29–7.25 (m, 1H), 7.19–7.17 (m, 2H), 4.11–3.98 (m, 2H), 3.77–3.69 (m, 2H), 2.72–2.66 (m, 1H), 2.55 (bs, 1H), 2.49–2.42 (m, 1H), 2.19–2.11 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 151.8, 142.9, 140.4, 128.9, 128.4, 126.2, 61.3, 47.6; HRMS (ESI-MS): Calcd. for C₁₂H₁₅N₃O (M+H): 218.1293, Found: 218.1302.

**X-rays crystallography of 3i (CCDC 1975292)**

A single crystal of 3i was obtained from THF/n-Hexane solvent at room temperature. Diffraction data were collected on Bruker SMART Apex-III CMOS-Based X-ray diffractometer with Cu-Kα. Radiation (λ = 1.54178). The empirical absorption correction was applied by using the SADABS program. The structure was solved using direct method, and refined by full matrix least-squares on F² (G.M Sheldrick, SHELXL2014, program of crystal structure refinement, University of Göttingen, Germany).

**Table 1. Crystal data and structure refinement for 3i**

<table>
<thead>
<tr>
<th>Identification code</th>
<th>3i</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₁₂H₁₂BrN₃O</td>
</tr>
<tr>
<td>Formula weight</td>
<td>294.16</td>
</tr>
<tr>
<td>Temperature</td>
<td>296(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, P2(1)/n</td>
</tr>
</tbody>
</table>
Unit cell dimensions

\[a = 4.7996(13) \, \text{Å}\]
\[b = 9.8909(15) \, \text{Å}\]
\[c = 26.029(4) \, \text{Å}\]
\[\alpha = 90\, \text{deg.}\]
\[\beta = 92.99(2)\, \text{deg.}\]
\[\gamma = 90\, \text{deg.}\]

Volume
\[V = 1234.0(4) \, \text{Å}^3\]

Z, Calculated density
\[Z = 4,\, \text{1.583 Mg/m}^3\]

Absorption coefficient
\[\mu = 4.444 \, \text{mm}^{-1}\]

F(000)
\[592\]

Crystal size
\[0.180 \times 0.160 \times 0.150 \, \text{mm}\]

Theta range for data collection
\[3.400\, \text{to}\, 68.419\, \text{deg.}\]

Limiting indices
\[-5 \leq h \leq 5,\, -11 \leq k \leq 11,\, -30 \leq l \leq 31\]

Reflections collected / unique
\[14924 / 2262\, [R(int) = 0.0443]\]

Completeness to theta = 67.679
\[99.9\, \%\]

Refinement method
Full-matrix least-squares on \(F^2\)

Data / restraints / parameters
\[2262 / 0 / 156\]

Goodness-of-fit on \(F^2\)
\[1.025\]

Final R indices [I>2\sigma(I)]
\[R1 = 0.0462, \, wR2 = 0.1139\]

R indices (all data)
\[R1 = 0.0652, \, wR2 = 0.1306\]

Extinction coefficient
n/a

Largest diff. peak and hole
\[0.369\, \text{and}\, -0.577 \, \text{e.Å}^{-3}\]

**Figure S1:** Molecular structure of 3i

**References:**


$^{19}$F NMR spectrum for 3f